

## **UNIT ONE**

# **ZEROTH LAW AND FIRST LAW OF THERMODYNAMICS**

### **Introduction**

Thermodynamics is the branch of physics which deals with processes involving heat, work and internal energy. In other words thermodynamics deals with the transformation of heat into mechanical work. Thermodynamics does not take into account the atomic constitution of matter but only deals with macroscopic properties of the system, such as pressure, volume, temperature, internal energy, etc., that we can observe and measure in experiments. There are mainly four laws in thermodynamics. They are zeroth law, first law, second law and third law of thermodynamics. The zeroth law of thermodynamics introduces the concept of temperature and thermodynamic equilibrium. The first law of thermodynamics gives the relation between heat and mechanical work and the second law which is the backbone of thermodynamics depicts the direction and manner in which heat flow takes place. The third law of thermodynamics explains the nature of bodies in the neighbourhood of absolute zero temperature. Finally, in short, we can say that thermodynamics is an experimental science and based upon the general laws of nature which govern the conversion of heat into mechanical work and vice versa. Before getting into the chapter in detail we give definitions and brief explanations of some of the terms used in thermodynamics such as system, surroundings, closed system, open system and isolated system.

### **System**

In natural science the study of any special branch of it begins with a separation of a restricted region of space or a finite portion of matter from its surroundings by means of a closed surface called the boundary. The region within the arbitrary boundary and on which the attention is focused is called the system. In other words **any portion of matter which is considered as separated from its surroundings is called a system.**

### **Surrounding**

**All things which are outside the system and influence its behaviour are known as surroundings.** It may be some other system.

Let a gas be filled in a cylinder fitted with a piston heated by a burner. Here the gas is the system while the piston and the burner are the surroundings.

Depending upon the type of interaction between the particles of the system and the surroundings we have the following types of systems.

**(i) Open system**

A system which can exchange matter and energy with the surroundings is called an open system.

For example in air compressor, air at low pressure enters and air at high pressure leaves the system. i.e., there is an exchange of matter and energy with the surroundings.

**(ii) Closed system**

A system which can exchange only energy with the surroundings is called a closed system.

For example a gas enclosed in a cylinder expands when heated and pushes the piston upward. Here the matter (gas) in the system remains constant.

**(iii) Isolated system**

A system which is both thermally and mechanically isolated from the surroundings is called an isolated system.

A thermally isolated system means no heat flows into or out of the system. For example a system (gas) enclosed by perfectly insulating walls.

A mechanically isolated system means a system enclosed by perfectly rigid walls so that its volume remains unchanged. i.e., no communication of energy with the surroundings.

When a system has been chosen our next task is to describe it in terms of quantities related to the behaviour of the system or its interactions with the surroundings or both. In general there are two points of view that may be adopted. One is the macroscopic point of view and the second one is the microscopic point of view.

**Macroscopic point of view**

Macroscopic point of view considers variables or characteristics of a system at large scale. i.e., we describe a system by specifying the quantities of mass, composition, volume, pressure, and temperature etc. These quantities are called macroscopic coordinates which refer to the large scale characteristics. In general macroscopic coordinates have the following properties.

- (i) They involve no special assumptions concerning the structure of a matter, radiation or fields.
- (ii) They are few in number needed to describe the system.

- (iii) They can be directly experienced by our sense of perception.
- (iv) They can be measured directly in the laboratory.

The study of a system under this category leads to thermodynamics. Thus thermodynamics is the branch of natural science that deals with the macroscopic properties of the system such as pressure, volume, temperature etc. Geometrical optics, mechanics, electricity, magnetism etc. are other macroscopic branches of natural science. The presence of temperature in our system of study distinguishes thermodynamics from other macroscopic branches mentioned above.

### Microscopic point of view

**The microscopic point of view considers variables or characteristics of a system at atomic level.** There are large number of variables that describe the internal structure of the system or associated with the constituent of the system. The study of a system under this category leads to statistical mechanics. Thus statistical mechanics is defined as the branch of science that deals with the microscopic characteristic of the system. The microscopic description of a system involves the following properties.

- (i) Assumptions are made concerning the structure of matter, fields or radiation.
- (ii) Many quantities are needed to describe the system.
- (iii) They cannot be experienced by our sense of perceptions.
- (iv) They cannot be measured directly in the laboratory.

### Macroscopic versus microscopic points of view

If we study a system either by macroscopic point of view or by microscopic point of view both yield same conclusions and results.

In macroscopic study pressure, volume temperature etc are fundamental quantities which can be measured directly in laboratories, whereas in microscopic study these are quantities that can be calculated theoretically from the microscopic behaviour of the system. Moreover in macroscopic study of systems we cannot derive the relationship between various macroscopic quantities from fundamental principles. Everything stems from experimental observations. But in microscopic study of systems we can derive every relationship from fundamental principles. For example  $PV = nRT$  is an experimentally proved relationship in macroscopic study. However this relationship can be derived in the realm of microscopic study of systems from fundamental principles.

The above discussion shows that the microscopic point of view goes much beyond the macroscopic view point. Microscopic point of view assumes several things

about the system, sometimes it may go beyond our sense of perceptions and imaginations. It assumes the structure of microscopic particles, their motion, their energy states, their interactions etc. and we develop a mathematical frame work and predict about our measurable quantities and also derive the relation between various quantities involved in the study. Inspite of all these the final justification should come from the macroscopic point of view, where everything is measurable.

### **Scope of thermodynamics**

We found that in dealing a system by macroscopic point of view, it constitutes a description of the large scale characteristic of a system by means of a few of its measurable quantities suggested by our sensory perceptions i.e., the description of a system by some of the observable quantities associated with the system is the starting point of all investigations in all branches of natural science. For example, we want to deal with the mechanics of a rigid body. Obviously we go for macroscopic point of view. Firstly we find out some observable variables (coordinates) such as position, centre of mass with respect to time: clubbing of position and time we get another observable quantity velocity. The centre of mass, position, time, velocity etc. are some of the measurable quantities called mechanical coordinates. These coordinates enable us determine potential energy and kinetic energy of the rigid body. i.e., it is the purpose of mechanics to find out the relations between different mechanical coordinates which are consistent with Newton's laws of motion.

In thermodynamics the situation is slightly different. Here we take observable variables associated with the internal state of the system as pressure, volume, temperature etc. These observable quantities called thermodynamic coordinates. These coordinates enable us to determine the internal energy of the system. i.e., it is the purpose of thermodynamics to find out the relations between different thermodynamic coordinates which are consistent with the fundamental laws of thermodynamics. Some important thermodynamic systems are air, steam, gasoline vapour and air, a vapour in contact with its liquid etc.

### **Thermal equilibrium and zeroth law**

This section deals with the analytic development of the concept of temperature. We found that a thermodynamic system (say gas) is described by specifying its coordinates such as the mass, the pressure, the volume and the temperature. To simplify our discussion we shall deal only with systems of constant mass. For a given mass of gas and constant temperature, the thermodynamic coordinates are the pressure and the volume. May different values of pressure and volume are possible for a gas. If the pressure is kept constant, the volume may vary over a wide range of

values. If the volume is kept constant pressure may vary over a wide range of values. This shows that for a given mass of gas and constant temperature two independent coordinates (pressure and volume) are required to specify a thermodynamic system. It may be noted that though pressure and volume are independent but are related through Boyle's law ( $PV = \text{constant}$ ). In general we can say that X and Y are two independent coordinates to specify a thermodynamic system.

### Equilibrium state of a system

**A state of a system in which the coordinates X and Y have definite values that remain constant so long as the external conditions are unchanged is called an equilibrium state.** Or if there is no change in coordinates, by which the system is specified, of the system with respect to time is called an equilibrium state.

Suppose we have two systems A (described by specifying its coordinates as X, Y) and B described by specifying its coordinates as (X', Y') separated by a wall. How is, then, equilibrium of the two be defined. Obviously the equilibrium of the systems depends upon the nature of the wall. If we use an adiabatic wall for separation an equilibrium state for system A may coexist with any equilibrium state of B for all attainable values of the four quantities X, Y and X', Y'. See figure 1.1(a). This is because an adiabatic wall prevents two systems from communicating each other. Examples of adiabatic walls are thick layers of wood, concrete asbestos, felt etc.

On the other hand if the systems are separated by a diathermic wall the values of X, Y and X', Y' will change spontaneously until an equilibrium state of the combined system is attained. Then the systems are said to be in thermal equilibrium with each other (see figure 1.1(b)). This is because a diathermic wall allows heat transfer from one system to another system. The most commonly used dia thermic wall is a thin metallic sheet

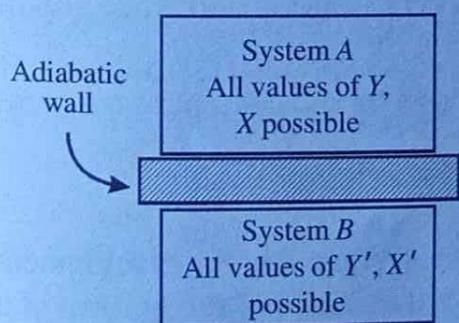


Figure 1.1(a)

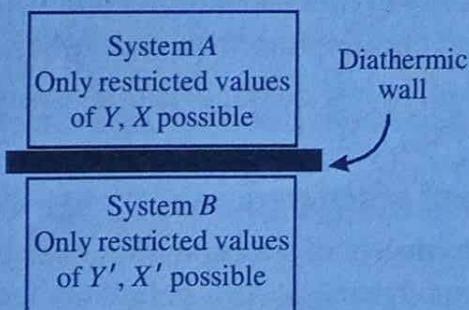
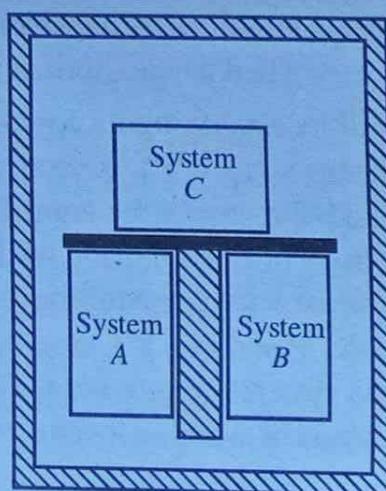


Figure 1.1(b)

### Zeroth law of thermodynamics

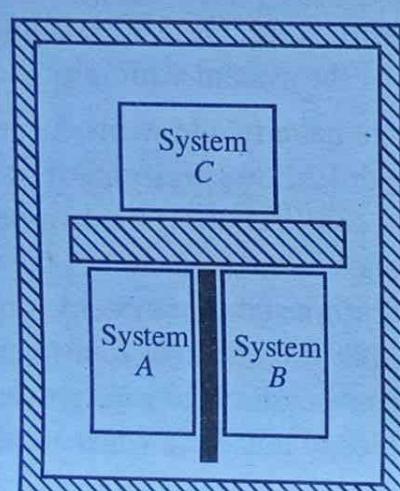
Imagine two systems A and B separated from each other by an adiabatic wall

obviously A and B are not in equilibrium. Suppose a third system C is brought in contact with both A and B through a diathermic wall. The entire system (A, B and C) is surrounded by an adiabatic wall (see figure 1.2(a)). After sometime A and C will be in thermal equilibrium and B and C will also be in thermal equilibrium. If the adiabatic wall separating A and B is replaced by a diathermic wall and the diathermic wall separating C from both A and B is replaced by an adiabatic wall (see figure 1.2(b)), we find that there is no further change. This means that the systems A and B are also in thermal equilibrium with each other. This is known as zeroth law of thermodynamics.



If A and B are each in thermal equilibrium with C

Figure 1.2(a)



A and B are in thermal equilibrium with each other

Figure 1.2(b)

### Statement

**Zeroth law of thermodynamics states that if two bodies A and B are each separately in thermal equilibrium with a third body C, then A and B are also in thermal equilibrium with each other.**

Zeroth law of thermodynamics establishes the basis for the concept of temperature.

### Concept of temperature

The concept of temperature is one of the basic tools required in the development of thermodynamics. As a definition, **temperature is a measure of the hotness of a given macroscopic object as felt by the human body.**

Defining temperature in this manner has lost its significance, relevance and the origin of it. But we require a scientific understanding of the concept of temperature. It is built upon thermal equilibrium established in zeroth law of thermodynamics.

Consider a system A in the state  $X_1, Y_1$  in thermal equilibrium with another system B in the state  $X'_1, Y'_1$ . Suppose we change the state of the system A to  $X_2, Y_2$  that is in thermal equilibrium with  $X'_1, Y'_1$  of system B. Experiment shows that there exists a set of states  $(X_1, Y_1), (X_2, Y_2), (X_3, Y_3) \dots$  etc. of system B all are in thermal equilibrium with  $(X'_1, Y'_1)$  of system B. According to zeroth law thermodynamics all states of A are in thermal equilibrium with one another. Now we plot a graph between X and Y of the state. It is seen that the set of states of A lie along a curve I as shown in figure 1.3(a). This curve is called an isotherm. Thus **isotherm is defined as the locus of all points representing states in which a system is in thermal equilibrium with one state of another system.**

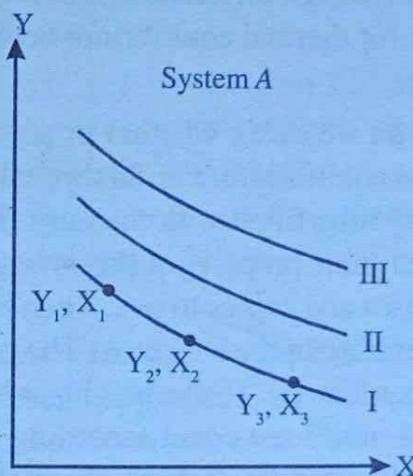


Figure 1.3(a)

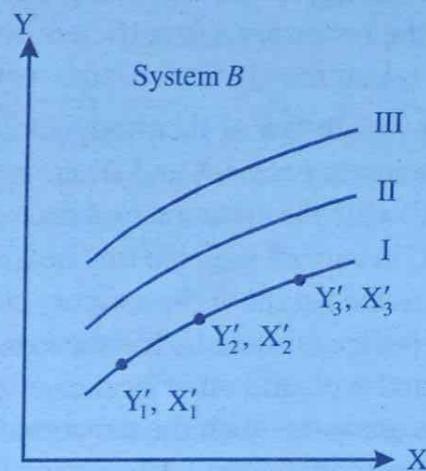


Figure 1.3(b)

#### Isotherms of two different systems

In a similar way we can find a set of states  $(X'_1, Y'_1), (X'_2, Y'_2), (X'_3, Y'_3) \dots$  etc. of the system B all of which are in thermal equilibrium with one state  $(X_1, Y_1)$  of A and therefore in thermal equilibrium with another according to zeroth law of thermodynamics. Plotting a graph between  $X'$  and  $Y'$  of the state, it is seen that the set of states of B lie along a curve called isotherm represented by I' as shown in figure 1.3(b). From zeroth law, it follows that all the states on isotherm I of system A are in thermal equilibrium with all the states on isotherm I' of system B.

The experiment is repeated with different starting conditions (of X, Y), we get a family of isotherms I, II, III ..... of system A and I', II', III' ..... of system B.

Take the isotherms I and I' each state of set A are in thermal equilibrium with one another and also in thermal equilibrium with each one of set B.

This statement indicates that the two systems have something in common. This common property which makes the systems in equilibrium in themselves also with one another.

We call this property temperature. Now we are in a position to define temperature scientifically. **The temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems.**

Temperature is a scalar quantity. This may be established on the basis of zeroth law of thermodynamics. For systems A and B to be in thermal equilibrium all the information that is needed is that both A and B are thermal equilibrium with another system C. We know that a scalar quantity is represented by a number. We can assign a number to each corresponding isotherms (say I and I') with the help of a set of rules. For different corresponding isotherms we assign different number. Once this is done, the necessary and sufficient condition for thermal equilibrium between two systems is that they have the same temperature.

Using zeroth law of thermodynamics how do we check whether or not two beakers of water (systems A and B) are in thermal equilibrium. For this we take a third system C which is an unmarked glass capillary tube filled with mercury. Bring the system C in contact with the first beaker A then some property of the device (system C) such as the height of the mercury column rises and comes to rest. Then by definition the device (system C) has the same temperature in the beaker A. The procedure is repeated with the other beaker of water (system B). If the heights of mercury columns are same then the temperatures of A and B are equal according to zeroth law of thermodynamics. The device (system C) used to establish thermal equilibrium is called a thermometer. In order to assign a numerical value to the temperature we perform experiments on standard system.

### Ideal gas temperature

In this section our aim is to see how to measure temperature. To measure a physical quantity we need some standard reference of the same kind. The standard reference chosen must be highly precise and accurately reproducible and must be invariant with time, place and environmental conditions. In olden days mercury thermometer was used as standard reference subjected to certain rules. However in the nineteenth century it was realised that gas thermometers are far better than mercury thermometers. In the year 1887 international committee on weights and measures (CIPM) adopted gas thermometer as the standard reference.

The theoretical basis for gas thermometry lies in ideal gas equation

$$PV = nRT \quad \dots \dots (1)$$

where  $P$  is the pressure of the system of gas,  $V$  is the volume of the gas,  $n$  is the number of moles of gas and  $R$  is the molar gas constant. The temperature  $T$  is the theoretical thermodynamic temperature. In this section we show the experiment that yields reproducible and accurate empirical temperature  $\theta$  of a real gas. It may be noted that our governing equation is that of an ideal gas and we are going to measure real gas temperature ( $\theta$ ). How to achieve this, is the problem.

The ideal gas temperature ( $T$ ) is found using a constant volume gas thermometer (Jolly's bulb) as follows. A schematic diagram of a constant volume gas thermometer is shown in figure 1.4.

The gas is contained in the bulb B. The bulb B is connected to a mercury column through a capillary tube. There is a marking at the top of the mercury column called indicial point. By adjusting the height of the reservoir (raising or lowering) until the mercury column in M just touches the indicial point we can make the volume of the gas always constant. The pressure in the bulb is equal to atmospheric pressure plus the difference in height  $h$  between the two mercury columns M and M'.

$$\text{i.e., } P = P_{\text{atm}} + \rho gh$$

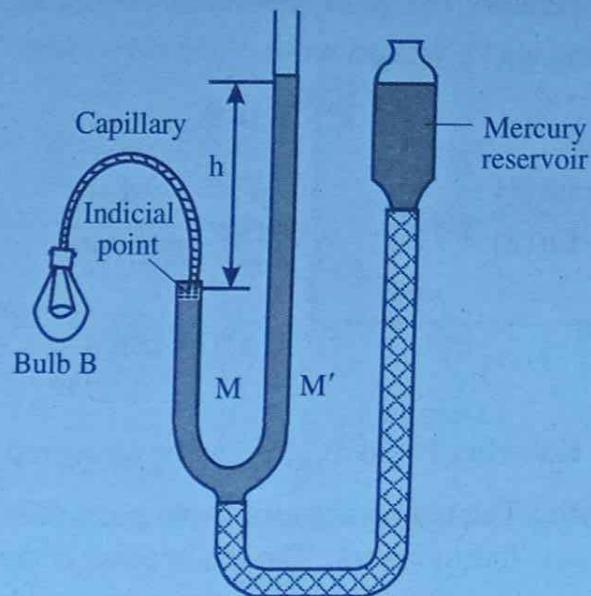
To begin the experiment the bulb is inserted in a triple point cell whose temperature is assigned as 273.16 K. Adjust the height of the reservoir until the mercury in the column M just touches the indicial point. Noting  $h$ , pressure of the gas  $P_{\text{TP}}$  is calculated.

Using equation (1), we can write

$$P_{\text{TP}} \propto 273.16 \text{ K} \quad \dots \dots (2)$$

(since volume of the gas is constant)

Remove the triple point cell and surround bulb with unknown real gas whose



**Figure 1.4 :** Constant volume gas thermometer. Mercury reservoir is raised or lowered so that the meniscus at the left always touches the indicial point. Bulb pressure equals  $h$  plus atmospheric pressure

temperature ( $\theta$ ) to be measured. As before measure the pressure inside bulb as  $P$ . Using eq(1), we can write

$$P \propto \theta \quad \dots \dots (3)$$

$$\frac{\text{Eq}(3)}{\text{Eq}(2)} \text{ gives} \quad \frac{P}{P_{TP}} = \frac{\theta}{273.16K}$$

$$\text{or} \quad \theta = 273.16K \frac{P}{P_{TP}} \quad \dots \dots (4)$$

Knowing  $P$  and  $P_{TP}$ ,  $\theta$  can be measured.

**Note :** The temperature of triple point (TP) of water is the standard fixed point of thermometry. The triple point is the temperature at which the solid, liquid and vapour phases coexist in equilibrium. A device that gives this temperature is called triple point cell.

Now we consider measuring ideal gas temperature ( $T$ ) at the normal boiling point (NBP) of water (The steam point). For this an amount of gas is introduced into bulb B and measure  $P_{TP}$  when the bulb is inserted in the triple point cell. Suppose that  $P_{TP}$  is equal to 120kPa. Keeping volume constant carry out the following procedure.

- Surround the bulb B with steam at standard atmospheric pressure, measure the gas pressure  $P_{NBT}$  as described earlier, then calculate the real gas temperature  $\theta$  using equation 4.

$$\text{i.e.,} \quad \theta(P_{NBP}) = 273.16K \frac{P_{NBP}}{120}$$

- Remove some of the gas from the bulb B so that  $P_{TP}$  has a smaller value (say 60 kPa). Measure the new value of  $P_{NBP}$  and calculate new value of  $\theta$ .

$$\theta(P_{NBP}) = 273.16K \frac{P_{NBP}}{60}$$

- Repeat the experiment by reducing the amount of gas step by step. Each time measure corresponding  $\theta$  value.

- (iv) Plot a graph between  $\theta(P_{NBP})$  against  $P_{TP}$ . Extrapolate the resulting curve to the axis where  $P_{TP} = 0$

From the graph we can measure

$$\text{LT } \theta(P_{NBP}) \Big|_{P_{TP} \rightarrow 0}$$

The whole experiment was repeated for three different gases, each time measured  $\theta(P)$  for the normal point of water. (see figure)

It is seen that although the readings of a constant volume gas thermometer depend upon the nature of the gas at ordinary values of  $P_{NBP}$ , all gases indicate the same pressure as  $P_{Tp} \rightarrow 0$ . Therefore we define the ideal gas temperature  $T$  by the equation

$$T = 273.16\text{K} \quad \text{Lt } \frac{P}{P_{TP} \rightarrow 0} \quad \text{constant V.} \quad \dots\dots (5)$$

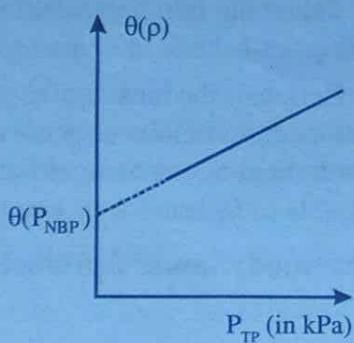


Figure 1.5

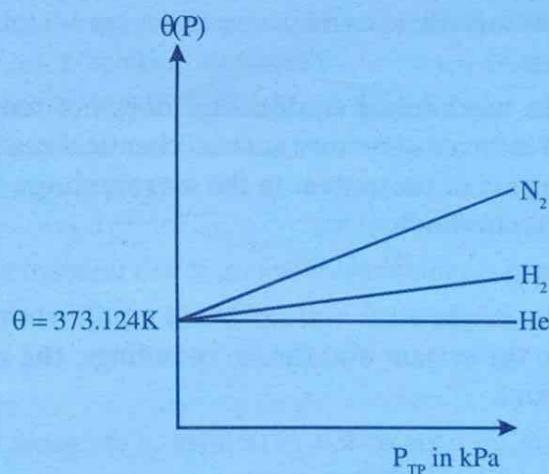


Figure 1.6

The above experiment shows that the behaviour of the real gases approaches the behaviour of ideal gas in limiting condition

i.e.,  $\theta = T$  when  $P_{Tp} \rightarrow 0$ .

This is our familiar statement that at low pressure and high temperature (NBP) all real gases behave like ideal gases.

Helium is the most useful gas for thermometric purposes for two reasons. At high temperatures helium does not diffuse, whereas hydrogen does. The second reason is that helium becomes liquid at a temperature lower than any other gas so that it is feasible to measure very low temperature than any other gas thermometers.

### **Thermodynamic equilibrium**

Suppose we want to conduct experiments on a thermodynamic system. Firstly identify two thermodynamic variables for the complete description of the macroscopic system. When these variables change either spontaneously or by outside influence the system is said to undergo change of state. When the system is not influenced in any way by its surroundings it is said to be an isolated system. These systems are of little use and importance. Usually we deal with systems influenced by its surroundings. The surroundings may exert forces on the system or provide exchange of energy. It is due to this interaction between the system and the surroundings the state of the system changes.

**When there is no resultant force or torque in the interior of the system and also none between the system and its surroundings, the system is said to be in a state of mechanical equilibrium** when these conditions are not satisfied the system undergoes change of state.

**When a system is in mechanical equilibrium does not tend to undergo a spontaneous change of internal structure such as chemical reaction or a transfer of matter from one part of the system to the surroundings, then the system is said to be in chemical equilibrium.**

When a system is not in chemical equilibrium, it will undergo change of state.

**When a system is in mechanical and chemical equilibrium, if it does not exchange heat between the system and the surroundings, the system is said to be in thermal equilibrium.**

In thermal equilibrium all parts of the system are at the same temperature and also the surroundings temperature. When these conditions are not satisfied the system will undergo change of state.

**When a system is mechanical, chemical and thermal equilibriums, the system is said to be in thermodynamic equilibrium.**

When a system is in thermodynamic equilibrium the variables (coordinates) representing the state of the system will not undergo change with respect to time.

It may be noted that thermodynamics does not deal with any problem involving time. However time factor plays a crucial role when we deal with kinetic theory of gases, hydrodynamics, chemical kinetics etc.

**When any one of the three conditions required for a system to be in thermodynamic equilibrium is not satisfied, the system is said to be in non equilibrium state.**

In non-equilibrium states as the thermodynamic variables change, the state of the system cannot be described by thermodynamic variables. Thus we are helpless in dealing with such systems partially. However approximation methods are available to deal with non-equilibrium states.

### **Equation of state**

For simplicity consider a closed system. A system (gas) enclosed in a cylinder provided with a piston. This being a closed system the matter (gas) remains constant and can exchange energy with the surroundings, we can very well measure the pressure P, the volume V and the temperature T of the system. If we fix P and V, automatically T will be fixed by nature. If V and T are fixed, the pressure P assumes a constant value. It shows among the three variables only two are independent variables. This implies that there exists an equation of equilibrium which connects the thermodynamic variables (coordinates). This is called an equation of state. Thus, **equation of state is a relation connecting between thermodynamical coordinates of the system in thermodynamic equilibrium.**

Equation of state in thermodynamics cannot be deducted theoretically but must come from experimental results. Thus the equation of state is valid only within the range of values measured experimentally. Beyond this range some other equation of state may come into play.

For example, the equation of state for an ideal gas is

$$PV = nRT$$

This is valid only at very low pressure.

At high pressures, the equation of state is Vander Waals equation given by

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \quad \dots\dots (6)$$

Where a and b are constants for a given gas but differ from gas to gas. The constant a takes into account particles interaction and b takes into account the finite size of the particles.

In both these equations of state three dynamical variables are used. This does not mean that these three variables ( $P$ ,  $V$ ,  $T$ ) are the only variables used to write equation of state. For example the relationship between the entropy ( $S$ ), the internal energy ( $U$ ) and pressure ( $P$ ) is as good as an equation of state as the above two equations. Therefore any two out of three can be chosen as independent variables, the third being a dependent variable. In general the three coordinates chosen is designated as  $X$ ,  $Y$  and  $Z$ . Such ZYZ systems will be called simple systems. PVT system is an important type of simple system.

### Hydrostatic systems

**Any isotropic system of constant mass and constant composition that exerts on the surroundings a uniform hydrostatic pressure in the absence of gravitation a electric and magnetic effects is called a hydrostatic system.**

Hydrostatic system is divided into three categories.

- (i) **A pure substance** : which is a single chemical compound in the form of a solid, a liquid, a gas, a mixture of any two or a mixture of all three
- (ii) **A homogeneous mixture of different compounds** such as a mixture of inert gases, a mixture of chemically active gases or mixture of liquids.
- (iii) **A heterogeneous mixture** such as mixture of gases in contact with a mixture of different liquids.

**Note :** An isotropic system means showing same property in all directions. A homogeneous system is a system which is completely uniform. When a system consists of two or more phases which are separated from one another by definite boundary surfaces is said to be a heterogeneous system.

It has been experimentally shown that the states of thermodynamic equilibrium of a hydrostatic system can be described in terms of three thermodynamic coordinates  $P$ ,  $V$  and  $T$ . i.e., every hydrostatic system is a PVT system, thus having an equation of state.

If the system undergoes a small change of state from its initial equilibrium state to very close equilibrium state, then all the coordinates ( $P$ ,  $V$ ,  $T$ ) undergo slight change. If the change in  $P$  is very small in comparison with  $P$  and very large in comparison with local fluctuations of pressure due to few number of molecule, then the change of  $P$  may be written as a differential  $dP$ . Similarly change in  $V$  is differential  $dV$  and that in  $T$  is  $dT$ . i.e., every infinitesimal change in thermodynamic coordinates (differential change) requires two conditions to be satisfied, that is the change is very small with respect to the quantity itself and large is in comparison with the effect produced by the behaviour of a few molecules. The reason for this is

that P, V and T refer to macroscopic behaviour. In other words thermodynamic system is a collection of an extra large number of particles.

The equation of state of a system is represented by expressed by a coordinate in terms of other two.

$$\text{Thus, } V = V(T, P)$$

Using the rule of partial differentiation, we can find the differential on both sides.

$$\text{i.e., } dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$$

Where the partial derivative  $\left( \frac{\partial V}{\partial T} \right)_P$  means the infinitesimal change in V with respect to infinitesimal change in T, keeping P constant. Similarly  $\left( \frac{\partial V}{\partial P} \right)_T$ . Both partial derivatives have an important physical meaning.

From the definition of average coefficient of volume expansion ( $\beta$ ) we have:

$$\text{Average coefficient of expansion} = \frac{\text{change in volume per unit volume}}{\text{change in temperature}}$$

where the changes occur at constant pressure.

$$\text{i.e., } \beta = \left( \frac{\Delta V}{V \Delta T} \right)_P = \frac{1}{V} \left( \frac{\Delta V}{\Delta T} \right)_P$$

When the change is made smaller and smaller it becomes infinitesimal.

$$\text{i.e., } \Delta V \rightarrow dV \text{ and } \Delta T \rightarrow dT.$$

$$\text{Thus } \beta = \frac{1}{V} \left( \frac{dV}{dT} \right)_P \quad \dots\dots (7)$$

Remember that  $\beta$  is a positive quantity since when T increases, V also increases except for water between  $0^\circ\text{C}$  and  $4^\circ\text{C}$ . This is because when temperature of water increases from  $0^\circ\text{C}$  to  $4^\circ\text{C}$ , volume decreases thereby  $\beta$  becomes negative. This is also true for rubber.

The unit of  $\beta$  is  $\text{K}^{-1}$ .

Similarly we recall the definition of average bulk modulus (B).

$$\text{Bulk modulus} = \frac{\text{change in pressure}}{\text{change in volume per unit volume}}$$

As before, for infinitesimal changes we can write

$$B = \frac{dP}{dV/V} = V \left( \frac{\partial P}{\partial V} \right)$$

But we know that a positive change in pressure produces a negative change in volume, we introduce a negative sign to make B a positive quantity.

$$\therefore B = -V \left( \frac{\partial P}{\partial V} \right)$$

Further we assume that changes occur at constant temperature. Then B is called isothermal bulk modulus

$$\text{i.e., } B = -V \left( \frac{\partial P}{\partial T} \right) \quad \dots \dots (8)$$

In thermodynamics we always go for measuring reciprocal of isothermal bulk modulus called isothermal compressibility denoted by  $k_T$

$$k_T = \frac{1}{(B)_T}$$

$$\text{i.e., } k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \dots \dots (9)$$

The unit of  $k_T$  is  $(\text{Pa})^{-1}$ . Equations 7 and 9 are very important in thermodynamics because on the L.H.S of equations we have experimentally measured quantities. From this we can calculate the change in thermodynamic coordinates on the R.H.S.

If the equation of state is

$$P = P(T, V)$$

we get

$$dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV.$$

If

$$T = T(P, V)$$

$$dT = \left( \frac{\partial T}{\partial P} \right)_V dP + \left( \frac{\partial T}{\partial V} \right)_P dV$$

To see the physical meaning of  $\left(\frac{\partial T}{\partial P}\right)_V$ , see example 1. The above discussion shows that for any closed system the expressions for  $dV$ ,  $dP$  and  $dT$  enable us to use an equation of thermodynamic equilibrium to solve it for any coordinate in terms (see example 2) of the other two. Since  $dP$ ,  $dV$  and  $dT$  are differentials of actual functions, they are called exact differentials.

Finally it may also be worth recalling two theorems on partial differentiation

$$(i) \quad \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y / \partial x)_z}$$

$$(ii) \quad \left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$$

The negative sign on the R.H.S of theorem (ii) comes simply because of the three coordinates only two are independent.

### Intensive and extensive coordinates

We found that quantities such as pressure (P), volume (V), temperature (T) etc. of the system which determine the state of a system are known as thermodynamical variables. Thermodynamical variables fall into two broad categories. They are (i) intensive variables and (ii) extensive variables.

Imagine a system in thermodynamic equilibrium to be divided into two equal parts each with equal mass. Those properties of each half of the system that remain the same are said to be intensive, those that are halved are called extensive.

Pressure, temperature, surface tension, viscosity, emf, electric field, magnetic etc. are intensive variables. Intensive variables are independent of mass of the system. It is a characteristic property of the system.

Volume, length, area, charge, internal energy, number of moles etc. are extensive variables. Extensive variables depend on the mass or size of the substance present in the system.

### Example 1

Show that  $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{k}$

**Solution**

We have

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \dots \dots (1)$$

and

$$k = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \dots \dots (2)$$

Eq(1) gives  
Eq(2)

$$\frac{\beta}{k} = -\left( \frac{\partial V}{\partial T} \right)_P \left/ \left( \frac{\partial V}{\partial P} \right)_T \right.$$

i.e.,

$$\frac{\beta}{k} = -\left( \frac{\partial V}{\partial T} \right)_P \cdot \left( \frac{\partial P}{\partial V} \right)_T$$

or

$$\frac{\beta}{k} = \left( \frac{\partial P}{\partial T} \right)_V$$

Used theorem (i) and (ii) of partial differentiation.

**Example 2**

A mass of mercury at standard atmospheric pressure and a temperature of about  $15^\circ\text{C}$  is kept at constant volume. If the temperature is raised to  $25^\circ\text{C}$  what will be final pressure.  $\beta = 1.81 \times 10^{-4} \text{ K}^{-1}$  and  $k = 4.01 \times 10^{-11} (\text{Pa})^{-1}$

**Solution**

$$T_i = 15 + 273 = 288 \text{ K}, \quad T_f = 25 + 273 = 298 \text{ K}.$$

From example 1, we have

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\beta}{k}$$

or

$$dP = \frac{\beta}{k} dT \quad \text{Integrating}$$

we get

$$\int_{P_i}^{P_f} dP = \frac{\beta}{k} \int_{T_i}^{T_f} dT$$

$$P_f - P_i = \frac{\beta}{k} (T_f - T_i)$$

$$P_f - P_i = \frac{1.81 \times 10^{-4} \times 10}{4.01 \times 10^{-11}} = 4.51 \times 10^7 \text{ Pa}$$

**Example 3**

The equation of state of an ideal gas is  $PV = nRT$ . Show that the volume expansivity  $\beta$  is equal to  $\frac{1}{T}$  also show that the isothermal compressibility is equal to  $\frac{1}{P}$ .

**Solution**

We have  $PV = nRT$  ..... (1)

Take the derivative on both sides with respect to  $T$ , keeping pressure constant, we get

$$P \left( \frac{\partial V}{\partial T} \right)_P = nR \quad \dots\dots (2)$$

equation 2 by 1 gives

$$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{T}$$

By definition L.H.S is  $\beta$

$$\therefore \beta = \frac{1}{T}$$

Now take the derivative equation (1) with respect to  $P$ , keeping temperature constant, we get

$$P \left( \frac{\partial V}{\partial P} \right)_T + V = 0$$

or  $P \left( \frac{\partial V}{\partial P} \right)_T = -V \quad \dots\dots (3)$

$\frac{\text{Eq}(3)}{\text{Eq}(1)}$  gives  $\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{V}{nRT}$

or  $-\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{V}{nRT} = \frac{V}{PV} = \frac{1}{P}$

By definition L.H.S is  $k_T$

i.e.,

$$k_T = \frac{1}{P}$$

#### Example 4

A block of copper at a pressure of 1 atm, a volume of  $100\text{cm}^3$  and a temperature of  $10^\circ\text{C}$  experiences a rise in temperature of  $5^\circ\text{C}$  and an increase in volume of  $0.005\text{cm}^3$ . Calculate the final pressure.  $\beta = 4.95 \times 10^{-5}\text{K}^{-1}$ ,  $k = 6.17 \times 10^{-12}(\text{Pa})^{-1}$

#### Solution

$$P_i = 10^5 \text{ Pa}, V_i = 100 \times 10^{-6} \text{ m}^3$$

$$T_i = 10 + 273 = 373 \text{ K}$$

$$T_f = 15 + 273 = 378 \text{ K}$$

$$V_f = (100.005) \times 10^{-6} \text{ m}^3$$

Our aim is to find the pressure coordinate. P is a function of V and T

$$P = P(T, V)$$

$$\therefore dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV$$

Substituting for  $\left( \frac{\partial P}{\partial T} \right)_V = \frac{\beta}{k}$

and  $\left( \frac{\partial P}{\partial V} \right)_T = -\frac{1}{kV}$

We get  $dP = \frac{\beta}{k} dT - \frac{1}{kV} dV$  Integrating, we get

$$P_f - P_i = \frac{\beta}{k} (T_f - T_i) - \frac{1}{k} \ln \frac{V_f}{V_i}$$

Substituting the values, we get

$$P_f - P_i = \frac{4.95 \times 10^{-5}}{6.17 \times 10^{-12}} \times 5 - \frac{1}{6.17 \times 10^{-12}} \ln \frac{100.005}{100}$$

$$P_f - P_i = 4.01 \times 10^7 - 16.21 \times 10^{10} \times \ln 1.00005$$

$$P_f - P_i = 4.01 \times 10^7 - 16.21 \times 10^{10} \times 4.99 \times 10^{-5}$$

$$P_f - P_i = 4.01 \times 10^7 - 80.89 \times 10^5$$

$$P_f - 1 \text{ atm} = 401 \text{ atm} - 80.89 \text{ atm}$$

$$P_f - 1 \text{ atm} = 320.11 \text{ atm}$$

$$P_f = 321.11 \text{ atm}$$

## Work

Whenever a system undergoes a displacement under the action of a constant force, work is said to be done. Work is measured as the product of force and the component of displacement parallel to the force

$$\text{i.e., } W = \vec{F} \cdot \vec{S} = F s \cos \theta$$

$$\text{If the force is variable work done is given by } W = \int \vec{F} \cdot d\vec{r}$$

If a system as a whole exerts a force ( $\vec{F}$ ) on the surroundings and a displacement ( $\vec{S}$ ) takes place, depending upon the direction of  $\vec{F}$  and  $\vec{S}$ , the work done is either by the system or on the system is called external work done. i.e., external work done is due to interaction between the system and the surroundings. For example a gas is enclosed in a cylinder provided with a piston. When the gas expands, it is imparting motion to the piston thereby doing work on its surroundings (piston). The work done by any part of the system on any other part is called internal work. It is due to interaction between the constituents (atom or molecules) of the system. Internal work done cannot be discussed in macroscopic thermodynamics. Thus in this chapter whenever we say work it implies external work.

When a system does external work parameters required to find the work done can be expressed in terms of thermodynamical variables specifying the system.

## Sign convention of work

In mechanics when a force exerts on a mechanical system in the same direction of displacement, work is positive and work is said to be done on the system. In this

case energy of the system increases. For thermodynamics to be consistent with mechanics, we adopt the same convention. Thus work is done on the system, work is considered as positive. When work is done by the system, work is considered as negative.

### Quasi static process

When a system is in thermodynamic equilibrium and the surroundings are kept unchanged, no motion will take place and no work will be done. If somehow there is an unbalanced force acting on the system, the mechanical equilibrium, thermal equilibrium and chemical equilibrium may upset, then the system will be no longer in thermodynamic equilibrium. This system will pass through non-equilibrium states, then the system will not be described by thermodynamic variables. To overcome this we imagine an ideal situation in which the unbalanced force is infinitesimal and the process proceeds infinitesimally slowly. A process performed in this ideal way said to be quasi-static. During a quasi-static process, the system is at all times infinitesimally close to a state of thermodynamic equilibrium.

**Thus a quasi-static process is a process in which a system successively changes from one equilibrium state to the next equilibrium state differing only infinitesimally from the first one.**

A quasi-static process is an ideal concept which can never be realised in the laboratory. However in the laboratory many processes approach quasi-static process with no significant error.

The introduction of the concept of quasi-static processes enable us to calculate the work done. In thermodynamics we deal with only reversible quasistatic processes only in which dissipative forces are ignored. It may be noted that all processes that we deal in thermodynamics are quasi-static.

Depending upon the conditions imposed on a given hydrostatic system it can undergo several types of processes such as quasi-static isothermal expansion or compression of an ideal gas, quasic-static increase of pressure on a solid, quasi-static expansion or compression of a gas in an adiabatic container, quasi-static isobaric process, quasi-static isochoric process, quasi-static cyclic process and quasi-static non cyclic process.

#### (i) Quasi-static isothermal process

A process in which pressure and volume change at constant temperature is known as an isothermal process. In such a process there is always heat transaction between the system and surroundings so that the system must be in very good thermal contact with surroundings. This means that the wall of the container is a perfect heat conductor (diathermic).

As an example let us consider a perfect gas enclosed in a cylinder of diathermic wall and equipped with a smooth piston. When the gas is compressed by pushing the piston inward, the work is done on the gas and its temperature increases. In order to keep the temperature constant, heat, equivalent to the work done, must flow out of the system. Similarly during an expansion process heat flows from surroundings to the system.

The equation of state for isothermal processes of a perfect gas is,

$$PV = \text{constant}$$

A graph between volume and pressure in an isothermal process is known as an *isothermal*.

Since the internal energy of a perfect gas depends only on temperature, the internal energy of a perfect gas remains constant in an isothermal process.

## (ii) Quasi-static adiabatic process

In adiabatic process, the system is isolated from the surroundings so that heat neither enters nor leaves the system. In this process pressure, volume and temperature may change. Obviously the system must be enclosed in a perfect insulator of heat.

Now let us consider a perfect gas enclosed in cylinder fitted with a piston. Both the cylinder and piston are made of perfect insulators of heat. Any change in the pressure and volume is always accompanied by a *temperature change*, since the work done in this case is converted as internal energy of the system.

Since perfect thermal isolation is not possible the quick and sudden processes are considered as adiabatic processes. The bursting of an inflated motor car tyre, the compression and expansion of the working substance during the compression stroke and power stroke respectively of a petrol engine or a diesel engine etc. are examples of adiabatic process. Since pressure, volume and temperature change in an adiabatic process we cannot draw a graph in a single plane. But we can show that at any point the adiabatic curve has a steeper negative slope than does an isothermal curve at the same point.

The equation of state for adiabatic processes of a perfect gas is

$$PV^\gamma = \text{constant}$$

where  $\gamma$  is the ratio of specific heats i.e.  $\gamma = \frac{C_p}{C_v}$

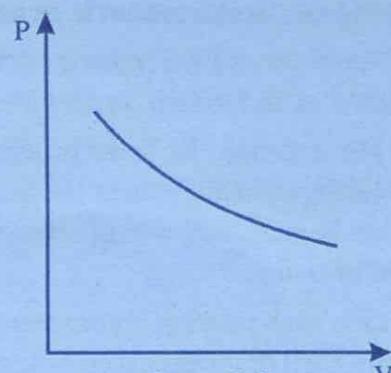


Figure 1.7

### (iii) Quasi-static isobaric process

A process taking place at constant pressure is known as an isobaric process.

For example isobaric process occurs in the boiler super heater where the heat of the existing steam is increased without increasing its associated pressure.

One such process is represented by a line AB in the P-V diagram given below.

### (iv) Quasi-static isochoric process

A process taking place at constant volume is called an isochoric process. It is also called as isometric process. For example addition or removal of heat from a system (gas) enclosed in a sealed non-deformation container. The ideal ottocycle is another example of isochoric process. When it is assumed that the burning of the gasoline-air mixture in an internal combustion engine car is instantaneous, there is an increase in temperature and pressure of the gas inside the cylinder while the volume remains constant. One such process is represented by the line BC in the P-V diagram given above.

### (v) Quasi-static cyclic process

Cyclic process is a process in which a system is taken from an initial state A ( $P_i, V_i, T_i$ ) to a succession of states but is always brought back to the initial state. Such a process is represented by a closed path in a P-V diagram (see figure 1.9).

It is obvious that there is no change in the state of the system at the end of a cycle in such a process. i.e.  $P, V, T, U, S$ , etc. remain unchanged at the end of a cycle. The internal energy  $U$  of the system depends only on the state of the system; so in a cyclic process the net change of internal energy  $dU$  will be equal to zero. i.e.,  $dU = 0$ .

The carnot cycle is the best example for a cyclic process. A devise that converts heat into mechanical work continuously by performing cyclic processes is known as a heat engine.

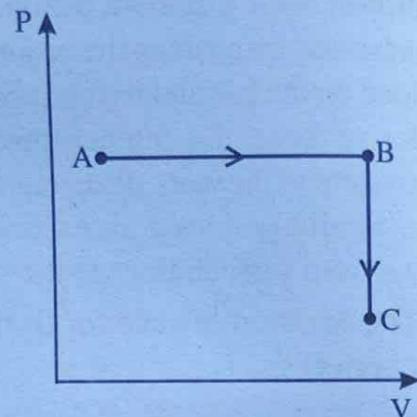


Figure 1.8

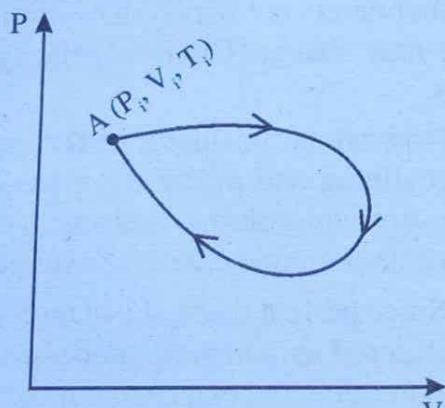


Figure 1.9

### (vi) Quasi-static non-cyclic process

A thermodynamic system which undergoes series of changes and does not come back to the original state is called as non-cyclic process.

A gas enclosed in a cylinder is compressed by a piston, if the piston does not come back to the original position, we can say gas undergoes a non-cyclic process.

### Work in changing the volume of hydrostatic system

Consider a system (gas) enclosed in a cylinder provided with a frictionless piston. Let A be the area of cross section of the cylinder. Let P be the pressure exerted by the system on the piston, therefore the corresponding force is PA. The surroundings also exert an opposing force on the piston. Let F be the force act on the system from the surroundings. The force F is slightly different from the force PA of the system. Under this condition the piston moves through an infinitesimal distance dx during compression. See figure below. The surroundings perform an infinitesimal work on the system (positive) denoted by  $dW$  (d-bar W)

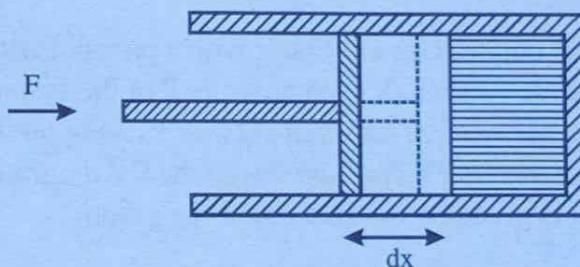


Figure 1.10

$$\text{Thus } dW = Fdx = PAdx$$

$dV = Adx$  infinitesimal change in volume. During compression the volume of the system decreases, so we put a negative sign before  $dV$ , this makes  $dW$  positive. Hence  $dW = -PdV$

Note that here P and V denote some intermediate stage of the quasistatic process. Integrating this we get the total work done during a finite quasistatic process in which volume changes from  $V_i$  to  $V_f$

$$W = - \int_{V_i}^{V_f} PdV \quad \dots\dots (10)$$

Since we perform a quasistatic process P is the thermodynamic coordinate. But we know that P is a function of V and T. Thus the above integration can be done

provided T is specified. When T is specified P is only function of V. When this is achieved, the path of integration through successive equilibrium states is defined.

Suppose T of a quasistatic process is specified (path specified) and going from an initial volume  $V_i$  to final volume  $V_f$  then work done is

$$W_{if} = - \int_{V_i}^{V_f} P dV$$

Along the same path we come back from volume  $V_f$  to  $V_i$ , then work done is

$$W_{fi} = - \int_{V_f}^{V_i} P dV$$

Comparing the two we get

$$W_{if} = -W_{fi}$$

### PV diagram

Consider a system (gas) enclosed in a cylinder with a piston. Piston is allowed to move. Each time measure the volume (V) and pressure P of the system. Plot a graph between pressure P along the vertical axis and volume V along the horizontal axis. The graph so obtained is called a PV diagram. From the PV diagram we can calculate the work done which is given by the area under the graph.

$$\text{i.e., } W_{if} = - \int_{V_i}^{V_f} P dV = \text{Area under the graph}$$

Various PV diagrams are shown in figure below.

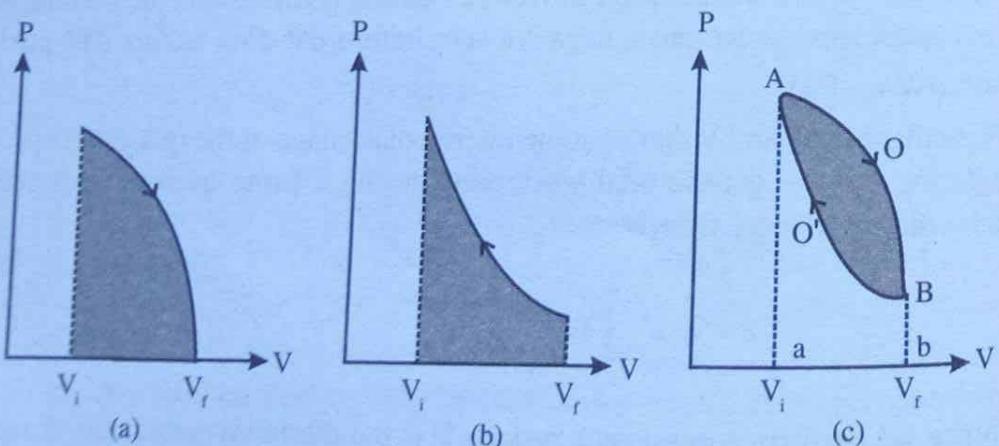


Figure 1.11

In figure 1.11(a),  $dV$  is positive since  $V_f > V_i$  so the work done is negative indicating work is done by the system.

In figure 1.11(b),  $dV$  is negative since  $V_f < V_i$  so the work done is positive means work is done on the system.

In figure 1.11(c), when the system goes from A to B,  $dV$  is positive, work done is negative. So work is done by the system given by the area AOBba. When the system moves from B to A,  $dV$  is negative, work done is positive, so work is done on the system given by BO'Aab. Since area AOBba is greater than BO'Aab network done is negative. This is given by the area of the shaded portion so in this closed path network is done by the system.

**Note :** Any two independent thermodynamic variables such as (P, V), (T, V) (P, T) and (T, S) can be chosen to draw diagrams. In general these diagrams are called indicator diagrams.

### Hydrostatic work depends on the path

Consider a hydrostatic system taken from state A to state B as shown in figure 1.2. Let the coordinates of state A and B be  $(P_1, V_1)$  and  $(P_2, V_2)$  respectively where  $P_1$  and  $V_1$  represent pressure and volume of state A and  $P_2$  and  $V_2$  that of state B. The system can move from A to B in different ways. We choose different paths such as AB, ADB and ACB. Our aim is to calculate the work done along these different paths which starts from A and ends at B in all cases.

- (a) Starting from point A, the pressure is continuously decreased from  $P_1$  to  $P_2$  along the line AB so that the volume increases from  $V_1$  to  $V_2$ . The work done by the system is given by

$$W_1 = \int_{V_1}^{V_2} P dV = \text{Area of the trapezium ABFE} = \frac{1}{2}(P_1 + P_2)(V_2 - V_1)$$

- (b) Starting from point A, the volume  $V_1$  is kept constant in going from A to D, the pressure decreases from  $P_1$  to  $P_2$  and then  $P_2$  is kept constant from D to B. The work done in this process (along the path ADB) is given by

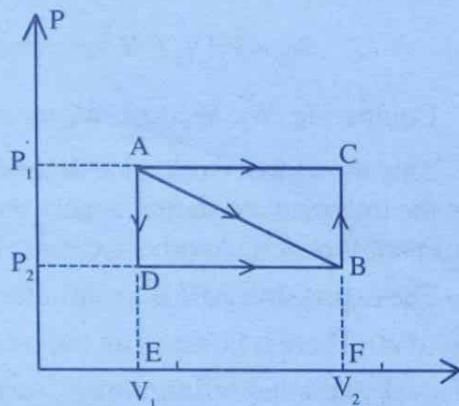


Figure 1.12

$$\begin{aligned} W_2 &= \text{Area under DBFE} \\ &= \text{Area of the rectangle DBFE} \end{aligned}$$

$$W_2 = P_2(V_2 - V_1)$$

[Remember that along the path AD, the process is isochoric hence work done along AD is zero. Along the path DB, the process is isobaric and the corresponding work done is  $P_2(V_2 - V_1)$ ]

- (c) Now we start from point A, the pressure  $P_1$  is kept constant in going from A to C and then the volume  $V_2$  is kept constant from C to B.

The work done along the path  $AC = P_1(V_2 - V_1)$  since the process is isobaric.

The work done along the path  $CB = 0$  since the process along this path is isochoric.

$\therefore$  The total work done along the path ACB,

$$W_3 = \text{work done along } AC + \text{work done along } CB$$

$$\text{i.e. } W_3 = P_1(V_2 - V_1) = \text{Area under ACFE}$$

Comparing  $W_1$ ,  $W_2$  and  $W_3$  we can see that  $W_1 \neq W_2 \neq W_3$ .

This shows that work done depends not only on the initial and final states but also on the intermediate states, namely on the path of integration. Thus we say that work is a path function. Another example for path function is heat.

The expression  $PdV$  is an infinitesimal amount of work and has been represented by  $(dW)$ . There is however an important distinction between an infinitesimal amount of work and other infinitesimals, such as  $dP$  or  $dV$ . An infinitesimal amount of thermodynamic work is an inexact differential that  $dW$  is not the differential of an actual function of the thermodynamic coordinates. To indicate that an infinitesimal amount of work is not a mathematical differential of a function  $W$  and to emphasise at all times that it is an inexact differential it is written as  $dW$

### Calculation of work for quasi-static process

#### Work done during quasi-static isothermal process

Consider a hydrostatic system (ideal gas) undergoes a quasi-static isothermal process from volume  $V_i$  to  $V_f$

The work done is given by

$$W = - \int_{V_i}^{V_f} P dV$$

The equation of state for an ideal gas is

$$PV = nRT$$

or

$$P = \frac{nRT}{V}$$

Substituting for P we get

$$W = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} \quad (\because T \text{ is constant})$$

$$W = -nRT \ln \frac{V_f}{V_i} \quad \dots\dots (11)$$

(See examples 5 and 6)

Work done can also be expressed in terms of  $P_i$  and  $P_f$

For isothermal process, we have

$$PV = \text{constant}$$

i.e.,

$$P_i V_i = P_f V_f$$

or

$$\frac{V_f}{V_i} = \frac{P_i}{P_f}$$

Now equation 11 becomes

$$W = -nRT \ln \frac{P_i}{P_f} \quad \dots\dots (12)$$

or

$$W = nRT \ln \frac{P_f}{P_i}$$

### Work done during isothermal increase of pressure on a solid

Consider a hydrostatic system (solid) undergoes an isothermal process from pressure  $P_i$  to  $P_f$ . The work done is given by

$$W = - \int_{P_i}^{P_f} P dV \quad \dots \dots (13)$$

This integral cannot be performed since it is a two variable integration. Fixing the path of integration we can proceed. Here the path of integration is determined by isothermal compressibility.  $V$  is a function of  $P$  and  $T$

i.e.,  $V = V(P, T)$

$$dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT$$

Since the process is isothermal, the second term goes.

$$\therefore dV = \left( \frac{\partial V}{\partial P} \right)_T dP$$

or  $dV = -kVdP \quad \dots \dots (14)$

$$\therefore k = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T, k \text{ is the isothermal compressibility.}$$

Substituting eq 14 in eq 13 we get

$$W = \int_{P_i}^{P_f} P k V dP$$

At constant temperature,  $k$  and  $V$  are almost constant, thus

$$W \approx kV \int_{P_i}^{P_f} P dP = kV \frac{P^2}{2} \Big|_{P_i}^{P_f}$$

$$W \approx \frac{kV}{2} (P_f^2 - P_i^2) \quad \dots \dots (15)$$

(see examples 7 and 8)

### Work done during a quasi-static adiabatic process

Consider a hydrostatic system (ideal gas) undergoes an quasi-static adiabatic process where system goes from initial state ( $P_i, V_i$ ) to final state ( $P_f, V_f$ ). The work done is given by

$$W = - \int P dV$$

For an adiabatic process the equation of state of an ideal gas

$$PV^\gamma = K, \quad K \text{ is a constant}$$

$$\text{or} \quad P = \frac{K}{V^\gamma}$$

$$\therefore W = - \int_{V_i}^{V_f} \frac{K}{V^\gamma} dV = -K \int_{V_i}^{V_f} V^{-\gamma} dV$$

$$W = -K \frac{V^{-\gamma+1}}{-\gamma+1} \Big|_{V_i}^{V_f} = \frac{K}{\gamma-1} (V_f^{-\gamma+1} - V_i^{-\gamma+1})$$

Using  $P_i V_i^\gamma = K$  and  $P_f V_f^\gamma = K$

We get

$$\begin{aligned} W &= \frac{1}{\gamma-1} [KV_f^{-\gamma+1} - KV_i^{-\gamma+1}] \\ W &= \frac{1}{\gamma-1} [P_f V_f^\gamma V_f^{-\gamma+1} - P_i V_i^\gamma V_i^{-\gamma+1}] \\ W &= \frac{1}{\gamma-1} [P_f V_f - P_i V_i] \end{aligned} \quad \dots\dots (16)$$

(See example 9 and 10)

The above equation can also be written in terms of temperatures. For ideal gas, the gas law can be applied to all processes.

We have  $PV = nRT$

$$\begin{aligned} P_i V_i &= nRT_i \\ \text{and } P_f V_f &= nRT_f \end{aligned}$$

Thus equation 16 becomes

$$W = \frac{nR}{\gamma - 1} (T_f - T_i) \quad \dots\dots (17)$$

(See problem - 16)

### Example 5

Two moles of an ideal gas kept at a constant temperature of 20°C changes its volume from 4 litres to 1 litre. Calculate the work done.

#### Solution

$$n = 2 \quad T = 20 + 273 = 293\text{K}$$

$$V_i = 4 \times 10^{-3} \text{ m}^3 \quad V_f = 1 \times 10^{-3} \text{ m}^3$$

$$\begin{aligned} \text{Using } W &= -nRT \ln \frac{V_f}{V_i} = -2 \times 8.315 \times 293 \ln \left( \frac{1}{4} \right) \\ &= 6753\text{J} \end{aligned}$$

Positive work indicates that work is on the gas.

### Example 6

Calculate the work done when one mole of an ideal gas expands isothermally at 27°C to double its original volume.  $R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$ .

#### Solution

$$n = 1, T = 27 + 273 = 300\text{K}$$

$$V_i = V, V_f = 2V$$

$$\text{Using } W = -nRT \ln \frac{V_f}{V_i}$$

$$W = -1 \times 8.315 \times 300 \times \ln \frac{2V}{V}$$

$$W = -8.315 \times 300 \times 0.693$$

$$W = -1728.7\text{J}$$

Negative work indicates that work is done by the system.

### Example 7

The pressure on 10 gram of solid copper is increased quasistatically and isother-

mally at 20°C from 0 to 1000 atm calculate the work done.  $\rho = 8.96 \times 10^3 \text{ kgm}^{-3}$ ,  $k = 7.16 \times 10^{-12} (\text{Pa})^{-1}$  and 1 atm =  $1.01 \times 10^5 \text{ Pa}$ .

### Solution

$$m = 10\text{g} = 10 \times 10^{-3} \text{ kg} = 10^{-2} \text{ kg}$$

$$T = 20 + 273 = 293\text{K}$$

$$P_i = 0, P_f = 100 \times 1.01 \times 10^5 = 1.01 \times 10^8 \text{ Pa}$$

$$\text{Using } W \approx \frac{kV}{2} (P_f^2 - P_i^2)$$

$$W \approx \frac{km}{2\rho} (P_f^2 - P_i^2)$$

$$W \approx \frac{7.16 \times 10^{-12} \times 10^{-2}}{2 \times 8.96 \times 10^3} [1.01 \times 10^8]^2 - 0$$

$$W \approx 4.076 \text{ J}$$

Positive work done indicates that work is done on the copper.

### Example 8

The pressure on 100g of nickel is increased quasistatically and isothermally from 0 to 500 atm. Assuming the density and isothermal compressibility to remain constant at values of  $8.90 \times 10^3 \text{ kgm}^{-3}$  and  $6.75 \times 10^{-12} (\text{Pa})^{-1}$  respectively. Calculate the work.

### Solution

$$m = 100\text{g} = 100 \times 10^{-3} = 10^{-1} \text{ kg}$$

$$P_i = 0, P_f = 500 \times 1.01 \times 10^5 \text{ Pa}$$

$$\text{Using } W \approx \frac{kV}{2} (P_f^2 - P_i^2)$$

$$W \approx \frac{km}{2\rho} (P_f^2 - P_i^2)$$

$$W \approx \frac{6.75 \times 10^{-12} \times 10^{-1}}{2 \times 8.90 \times 10^3} (5 \times 1.01 \times 10^7)^2$$

$$W \approx 9.671 \times 10^{-2} \text{ J}$$

Positive work indicates that work is done on the nickel.

### Example 9

A diatomic ideal gas of volume  $10^{-3} \text{ m}^3$  at a pressure of  $10^6 \text{ Pa}$  undergoes quasi static adiabatic process until the pressure drops to  $2 \times 10^5 \text{ Pa}$  and volume drop to  $3.16 \times 10^{-3} \text{ m}^3$  calculate the work.

### Solution

$$\gamma = 1.4, V_i = 10^{-3} \text{ m}^3, V_f = 3.16 \times 10^{-3} \text{ m}^3$$

$$P_i = 10^6 \text{ Pa}, P_f = 2 \times 10^5 \text{ Pa}.$$

Using  $W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$

$$W = \frac{2 \times 10^5 \times 3.16 \times 10^{-3} - 10^6 \times 10^{-3}}{1.4 - 1}$$

$$W = \frac{6.32 \times 10^2 - 10^3}{0.4}$$

$$W = -920 \text{ J}$$

Negative work indicates that work is done by the system.

### Example 10

A mono atomic ideal gas of volume 1 litre at a pressure of 8 atmospheres undergoes quasi-static adiabatic expansion until the pressure drops to 1 atm. How much work is done.  $1 \text{ atm} = 10^5 \text{ Pa}$ .

### Solution

$$V_i = 10^{-3} \text{ m}^3, V_f = ?$$

$$P_i = 8 \times 10^5 \text{ Pa}, P_f = 10^5 \text{ Pa}$$

$$\gamma = \frac{5}{3} \text{ (For a mono atomic gas)}$$

For an adiabatic process

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$V_f = \left( \frac{P_i V_i^\gamma}{P_f} \right)^{\frac{1}{\gamma}}$$

$$V_f = \left( \frac{P_i}{P_f} \right)^{\frac{1}{\gamma}} V_i$$

$$V_f = \left( \frac{8 \times 10^5}{10^5} \right)^{3/5} \cdot 10^{-3} = (8)^{3/5} \times 10^{-3}$$

$$V_f = 3.48 \times 10^{-3} \text{ m}^3.$$

∴ Work done is

$$W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

$$W = \frac{10^5 \times 3.48 \times 10^{-3} - 8 \times 10^5 \times 10^{-3}}{\frac{5}{3} - 1}$$

$$W = \frac{3.48 \times 10^2 - 8 \times 10^2}{2/3}$$

$$W = \frac{348 - 800}{2/3} = -6785$$

Negative work indicates that work is done by the system.

### Example 11

Calculate the work done upon expansion of one mole of a real gas quasistatically and isothermally from 10 litres to 22.4 litres at 20°C.  $a = 1.4 \times 10^9 \text{ Nm}^4 \text{ mol}^{-1}$  and  $b = 3.2 \times 10^{-5} \text{ m}^{-3} \text{ mol}$ .

**Solution**

For one mole of real gas equation of state is

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

or  $P = \frac{RT}{V-b} - \frac{a}{V^2}$

The work done,  $W = - \int_{V_i}^{V_f} P dV$

$$W = - \int_{V_i}^{V_f} \frac{RT}{V-b} dV + \int_{V_i}^{V_f} \frac{a}{V^2} dV$$

$$W = -RT \ln(V-b) \Big|_{V_i}^{V_f} - \frac{a}{V} \Big|_{V_i}^{V_f}$$

$$W = -RT \ln \frac{(V_f-b)}{(V_i-b)} - a \left( \frac{1}{V_f} - \frac{1}{V_i} \right)$$

Substituting the values, we get

$$W = -8.315 \times 293 \times \ln \frac{(10^{-2} - 3.2 \times 10^{-5})}{(22.4 \times 10^{-3} - 3.2 \times 10^{-5})}$$

$$-1.4 \times 10^9 \left( \frac{1}{22.4 \times 10^{-3}} - \frac{1}{10^{-2}} \right)$$

$$W = -2436.3 \ln \frac{9.968 \times 10^{-3}}{0.0224} - 1.4 \times 10^9 (44.64 - 100)$$

$$W = -2436.2 \ln (0.445) + 1.4 \times 10^9 \times 55.36$$

$$W = -2436.2 \times -0.81 + 77.5 \times 10^9$$

$$W = 1973.3 + 77.5 \times 10^9$$

$$W \approx 77.5 \times 10^9 J$$

## Work and heat

In the last section we found that a system can change its state by performing work done. But there are other means of changing the state of the system that do not involve performance of work. For example water containing in a heater with diathermic bottom is heated, the state of the system (water) changes. This happens because heater is at higher temperature and water is at a lower temperature. The temperature of a body has been assigned a meaning similar to level of a liquid. If there is a level difference liquid flows. Similarly if there is a temperature difference something flows. This something is called heat. In other words temperature is a measure of heat level. For example when two differently heated bodies are put in contact heat flows from one to the other. We know that it is because of temperature difference between the two bodies heat flows. Heat flows from a higher temperature to lower temperature until the two bodies attain a common temperature. Thus we define temperature as the thermal state of a body with reference to its ability to communicate heat to other bodies.

**Heat is defined as something which flows from one body at a higher temperature to the one at a lower temperature.**

In our example heat flow is the agency which changes the state of our system (water). This agency (heat) cannot be described by as mechanical work. The above discussion shows that work and heat are different agencies that cause the system to changes.

Finally it may be noted that an adiabatic wall does not allow heat to pass through, where as a diathermic wall transmits heat. In the mechanics a rigid wall does the function of adiabatic wall in heat. Rigid wall does not allow work. Through where as adiabatic wall does not allow heat to pass. A movable wall allows to perform work in mechanics where as a diathermic wall allows heat flow.

## Adiabatic work

Consider a closed system surrounded by adiabatic walls. For example a gas is enclosed in a cylinder with adiabatic walls provided with adiabatic piston. Since the system is surrounded by adiabatic walls no heat transfers from the system to the surroundings. However since it being a closed system it can exchange energy with the surroundings. i.e., the system experiences the process of working. This is called adiabatic work.

During adiabatic work the system moves from one state to another. The system can assume several paths to go from initial to final state. It has been experimentally verified by several experiments that the adiabatic work is same for all paths.

i.e., If a closed system is caused to change from an initial state to final state by adiabatic means only, then the work done is the same for all paths connecting the two states.

This statement enables us to draw an important conclusion. Recall from mechanics that when work done is independent of path, the force involved is said to be conservative, then there exists an associated function called potential energy function

$$F = -\frac{dU}{dr}$$

$$U_f - U_i = - \int_i^f \vec{F} \cdot d\vec{r}$$

In a similar way we can argue that our adiabatic work is independent of path but depends only on the initial state and the final state of the system then there exists a function called internal energy function denoted by  $U$ .

$$\text{i.e., } W_{i \rightarrow f} (\text{adiabatic}) = U_f - U_i \quad \dots \dots (18)$$

If  $W$  is positive then  $U_f > U_i$

It may be noted that thermodynamic work in general is path dependent but adiabatic work is path independent.

### Internal energy function

Experiments on adiabatic work brings us two informations one is that during an adiabatic process work done results in change of internal energy of the system. It is nothing but law of conservation of energy. The second is that adiabatic work introduces a new energy function associated with the system. The internal energy is a function which depends on many thermodynamic variables used to describe the system. For example a closed hydrostatic system is described by  $P$ ,  $V$  and  $T$ . so  $U$  is also a function of  $P$ ,  $V$  and  $T$ . But only two variables are required to specify a system, we keep the third one constant. In this situation  $W$  can be a function of  $(P, V)$ ,  $(T, V)$  and  $(T, P)$ .

$$U = U(T, V)$$

$$U = U(T, P)$$

and

$$U = U(P, V)$$

Taking the differentials, of first two we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

and       $dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP.$

The four partial derivatives have different physical meanings.  $\left(\frac{\partial U}{\partial T}\right)_V$  and  $\left(\frac{\partial U}{\partial T}\right)_P$  give the specific heat capacity of the system at constant volume and pressure respectively. This concept will be introduced soon.  $\left(\frac{\partial U}{\partial V}\right)_T$  tells us how does the internal energy of a system change with respect to change in volume keeping temperature constant.

$\left(\frac{\partial U}{\partial P}\right)_T$  tells us how does the internal energy of a system change with change in pressure keeping temperature constant.

It may be noted that it is not possible to measure the internal energy of a system but change in internal energy can be measured indirectly by measuring heat and work.

**Note :** For  $U = U(P, V)$  see example 15 and problem 13.

### Mathematical formulation of first law

We found that a system undergoes a change in state through the performance of adiabatic work only. This experiment is used only to measure the change in internal energy (eq 18). This is not the usual process carried out in laboratories. For example gas enclosed in a cylinder provided with adiabatic walls and a adiabatic piston. The bottom of the cylinder is provided with a diathermic boundary. When the system is heated at the bottom with a burner, the system undergoes a change in state by absorbing heat from the burner and does diathermic work (W). This is not equal to the adiabatic work  $U_f - U_i$ . Now we combine the two experiments firstly calculate  $U_f - U_i$  by doing adiabatic work, the system goes from state i to state f. Secondly perform the diathermic work such that the system goes from the same state i to the same state f.

Combining the effect of two experiments and use of law of conservation of en-

ergy we can define thermodynamic heat. It is defined as the **difference between the change in internal energy and diathermic work when a closed system undergoes a process in which diathermic work is done.**

Heat is denoted by  $Q$ . Thus we have

$$\begin{aligned} Q &= U_f - U_i - W \\ \text{or} \quad U_f - U_i &= Q + W \end{aligned} \quad \dots \quad (19)$$

This is known as the mathematical formulation of the first law of thermodynamics.

### Sign convention of $Q$

When heat enters a system  $Q$  is taken as positive and negative when heat leaves the system. Like  $U$  and  $W$ , heat is measured in joules.

### Significance of first law

- (i) It provides a method for determining the change in internal energy.
- (ii) It embodies the law of conservation of energy and
- (iii) it provides the definition of heat.

We found that heating is a process by which there is an exchange of energy between the system and the surroundings because of temperature difference. Now a fundamental question arises. What type of energy is exchanged. This can be precisely understood once the conditions of the processes are specified. Suppose we give heat to a system at constant volume it is called isochoric heat, which results in the transfer of internal energy. When heat is given to the system at constant pressure, it is called isobaric heat the heat (energy) transferred is known as enthalpy. It will be discussed later.

### Concept of heat

Heat is the flow of energy from one system to the other. Depending upon the conditions specified it could be either internal energy or enthalpy. During the flow of heat thermodynamic variables cannot be assigned to the system as it goes on changing. Thus heat cannot be expressed in terms of thermodynamic variables so the calculation of heat depends on the path of integration. Thus heat is an inexact differential. An infinitesimal change in heat is designated by  $dQ$ . When heat flow stops the system attains a new state, in this context the system can be represented by thermodynamic variables.

Imagine two systems A and B in thermal contact with each other and the composite system is surrounded by adiabatic walls.

For the system A alone

$$U_f - U_i = Q + W$$

For the system B alone

$$U'_f - U'_i = Q' + W'$$

Adding we get

$$(U_f - U_i) + (U'_f - U'_i) = Q + W + Q' + W'$$

$$\text{or } (U_f + U'_f) - (U_i + U'_i) = (Q + Q') + (W + W')$$

The equation represents the composite system. L.H.S represents the change in internal energy of the composite system.  $Q + Q'$  is the heat transferred to the composite system and  $W + W'$  is the work done for the composite system since the composite system is surrounded by adiabatic walls

$$Q + Q' = 0$$

$$\text{i.e., } Q = -Q'$$

It shows that within an adiabatic boundary heat lost (or gained) by the system A is equal to gained (or lost) by the system B. This is the basis of principle of method of mixtures. Experiments show that in general heat is not a conserved quantity but in an adiabatic container it is conserved.

**Note :** It is meaningless to say heat in a body or work in 'a body because both (Heat and work) are transient activities.

### Differential form of first law

When a thermodynamic system undergoes an infinitesimal process, the thermodynamic variables representing the system change infinitesimally. For such a process the first law of thermodynamics can be written as

$$dU = dQ + dW \quad \dots (20)$$

This is the mathematical form of first law.

For an infinitesimal quasistatic process  $dU$  and  $dW$  can be expressed in terms of thermodynamic coordinates only.

On the L.H.S of equation 20,  $dU$  is an exact differential whereas on the R.H.S both are inexact differentials. It should be noted that  $dU$  refers to a property within the system where  $dQ$  and  $dQ'$  are not related to the properties of the system rather they refer to the surroundings of the system and the interaction between the system and the surroundings.

For an infinitesimal quasistatic process of a hydrostatic system, we have  
 $dW = -PdV$ .

Now equation 20 becomes

$$dU = dQ - PdV$$

or

$$dQ = dU + PdV \quad \dots\dots (21)$$

### Heat capacity and its measurements

According to first law of thermodynamics we have

$$U_f - U_i = Q + W$$

This shows that internal energy can be changed either by heat ( $Q$ ) or work ( $W$ ). As it is easier to produce heat rather than work, we go with measuring  $U_f - U_i$  by supplying heat. Our aim is to measure the capability of a system to store internal energy by supplying heat to the system. Actually we are measuring internal energy capacity. Unfortunately this term had been miscoined as heat capacity.

Let  $\Delta Q$  be the heat given to a system and the corresponding change in temperature is  $\Delta T$ . Then, the average heat capacity is defined as

$$\text{Average heat capacity} = \frac{\Delta Q}{\Delta T}$$

In the limiting condition  $\Delta Q \rightarrow 0$  and  $\Delta T \rightarrow 0$ , the ratio approaches a limiting value known as heat capacity denoted by  $C$

$$\text{i.e.,} \quad C = \frac{dQ}{dT} \quad \dots\dots (22)$$

Its unit is  $\text{JK}^{-1}$ .

Remember that R.H.S is not a derivative of a function but simply a ratio.

The value of  $C$  depends on mass of the system because for a given  $dQ, dT$  will be different for different masses of the same system. In other words  $C$  is an extensive quantity. To make it intensive, we divide by mass  $m$ . Then the heat capacity is named as specific heat capacity denoted by  $c$

$$C = \frac{1}{m} \frac{dQ}{dT} \quad \dots\dots (23)$$

Its unit is  $\text{Jkg}^{-1}\text{K}^{-1}$ .

The adjective specific means per unit mass.

When specific heats of different substances are compared, no regularities found

to occur. However when the heat capacities are standardised to the same amount of substance called a mole, wonderful regularities found to occur.

The heat capacity per unit mole is called molar heat capacity. It is also denoted by  $c$ .

$$\text{i.e., } c = \frac{C}{n} = \frac{1}{n} \left( \frac{dQ}{dT} \right) \quad \dots \dots (24)$$

Its unit is  $\text{J mol}^{-1}\text{K}^{-1}$ .

The heat capacity can be negative, zero, positive or infinite depending upon the process of the system undergoes during heat transfer.

$$\text{We have } C = \frac{dQ}{dT}$$

For example, if a gas is compressed, its temperature rises, without supplying any heat to it. i.e.,  $dQ = 0$

$$\therefore C = \frac{0}{dT} = 0$$

On the other hand if a gas is allowed to expand without any rise in temperature i.e.,  $dT = 0$ , then

$$C = \frac{dQ}{0} = \infty$$

Thus in order to have a unique value of heat capacity of a hydrostatic system either by keeping pressure constant or volume constant.

Heat capacity at constant pressure is written as

$$C_p = \left( \frac{dQ}{dT} \right)_p$$

In general  $C_p$  is a function of  $P$  and  $T$ .

Heat capacity at constant volume is written as

$$C_v = \left( \frac{dQ}{dT} \right)_v$$

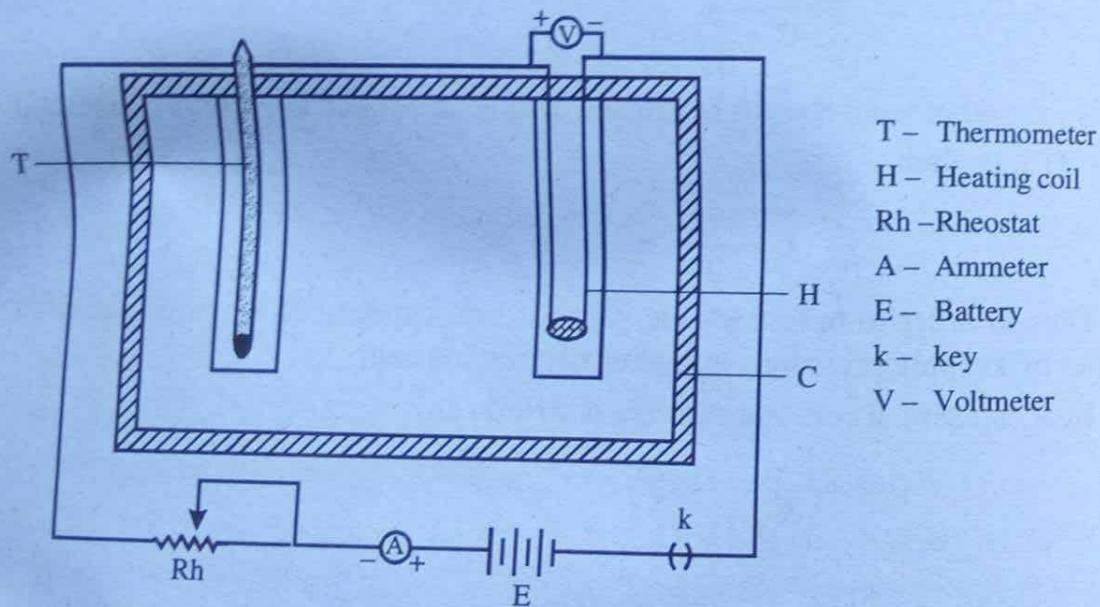
In general  $C_v$  is a function of  $V$  and  $T$ .

### Measurement of heat capacity

Measurement of heat capacities of solids, liquids and gases plays an important role in the realm of thermodynamics and statistical mechanics. In thermodynamics it enables us to categorize the substances and also gives other properties exhibited by them. Statistical mechanics is based on so many assumptions and the validity of their predictions should come from experimental measurements. Heat capacity is one among them.

Here we explain one of the classic methods of measurement of heat capacity called electric method.

To find the heat capacity of a solid, solid is taken in the form of a block. Two vertical grooves are made in the block as shown in the figure below. Measure the mass of the block after making the groove let it be  $m$ . A sensitive thermometer is kept in one of the grooves and a heating coil is in the other groove. The heating coil is connected to a rheostat, an ammeter, a battery and a key in series. A voltmeter is connected across the coil. The whole metal block is surrounded by thick cotton.



Pass a suitable constant current through the circuit. Measure the current from the ammeter and voltage from the voltmeter. Let it be  $I$ . Note the initial temperature as  $T_1$  from the thermometer. Start a stop watch every definite interval of time  $t$  note down the thermometer reading each time as  $T_2$ .

Heat delivered by the heating coil in time interval  $t_2 - t_1 = t$  is

$$dQ = VIt$$

This heat will be absorbed by the metal and the temperature rises. From the definition of heat capacity we have

$$dQ = m c dT$$

Comparing the two equations, we get

$$m c dT = V I t$$

or  $dT = \frac{VI}{mc} t$

Finally draw a graph between time interval on the horizontal axis and temperature difference along the vertical axis we get a straight line graph. The slope of the

graph gives  $\frac{dT}{t}$

i.e.,  $\frac{dT}{t} = \frac{VI}{mc}$

or  $c = \frac{VI}{m} \cdot \frac{1}{\text{slope}}$

knowing V, I, m and slope, we can calculate the specific heat capacity of the solid.

### Specific heat of water. The calorie

In olden days heat was measured in units of calorie (cal). One calorie is defined as the amount of heat required to raise the temperature by  $1^{\circ}\text{C}$  in a system of one gram of water. Later it was discovered that heat required to change the temperature of one gram of water from 0 to  $1^{\circ}\text{C}$  was different from the heat required to go from  $35^{\circ}$  to  $36^{\circ}$  (say). Calorie was then redefined as the heat required to raise the temperature of one gram of water from  $14.5$  to  $15.5^{\circ}\text{C}$ . Calorie is the unit of heat and unit of work is joule. They were considered as separate entities. Experiments showed that one can produce the other.

i.e.,  $W \propto H$

or  $W = JH$

Where J was called as the mechanical equivalent of heat. It was defined as the amount work done per unit mass of water in going from  $14.5^{\circ}$  to  $15.5^{\circ}\text{C}$ . The mechanical equivalent of heat was measured to be  $4.186 \text{ J cal}^{-1}$ . Later it was realised that mechanical equivalent of heat was nothing but specific heat of water, with joule as the unit of work. Now a days we never use mechanical equivalent of heat instead

we use specific heat of water. Then 1 calorie = 4.186 joules. The variation of specific heat of water with temperature is shown in figure below.

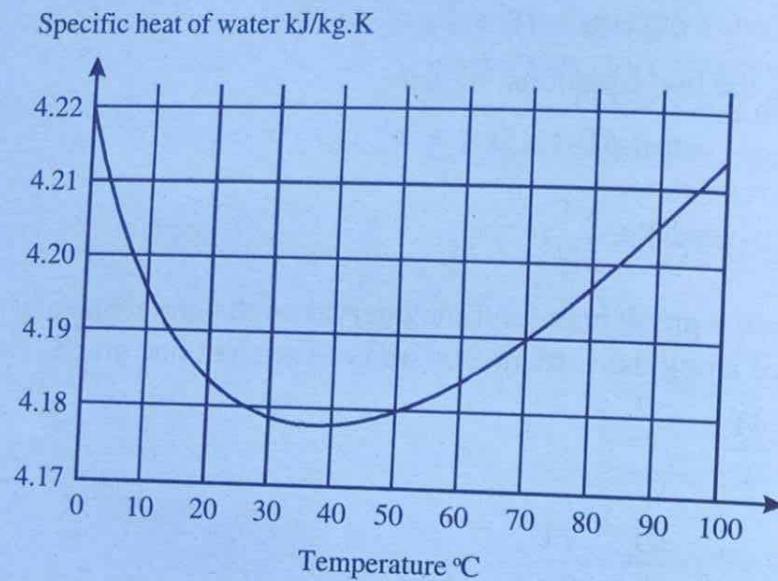


Figure 1.14 : Variation of specific heat capacity of water

### Quasistatic flow of heat: Heat reservoirs

In this section we shall explain how to accomplish quasistatic flow of heat. We found that when a system is not in thermodynamic equilibrium, it passes through several non equilibrium states hence system cannot be handled by thermodynamic coordinates. Likewise similar situation arises when there is a finite temperature difference between the system and the surroundings. As a result a non-uniform temperature distribution is set up in the system and handling this type of system is more complicated. However during a quasistatic process the difference between the temperature and the surrounding is infinitesimally small, system changes infinitesimally slow. The flow of heat is also infinitesimally small and the calculation can be performed in a simple way in terms of thermodynamic coordinates specifying the system.

To achieve a quasi-static flow of heat the system is put in contact with a heat reservoir. A heat reservoir is a body having infinite heat capacity and it may absorb or reject any amount of heat without changing its temperature appreciably. For example an ice cube is thrown into ocean will not produce a drop in temperature of the ocean. Another example is atmosphere. A flow of heat from a camp fire into the air will not produce a rise of temperature of the atmosphere. The ocean and atmosphere are examples of reservoirs.

Any system in contact with a reservoir undergoing quasi-static process is said to be isothermal and there is no flow of heat. To describe a quasi-static flow of heat involving a change of temperature the system has to be placed in contact successively with a series of reservoirs. Thus we imagine a series of reservoirs ranging in temperature from  $T_i$  to  $T_f$  placed successively in contact with a system at constant pressure in such a way that the difference in temperature between the system and the reservoir with which it is in contact is infinitesimal. The flow of heat will be quasi-static and can be calculated from the definition of heat capacity at constant pressure.

i.e.,

$$C_p = \left( \frac{dQ}{dT} \right)_p$$

or

$$Q = \int_{T_i}^{T_f} C_p dT$$

If  $C_p$  is constant

$$Q = C_p(T_f - T_i)$$

For a quasi-static isochoric process

$$C_v = \left( \frac{dQ}{dT} \right)_v$$

or

$$Q = \int_{T_i}^{T_f} C_v dT$$

If  $C_v$  is constant,  $Q = C_v(T_f - T_i)$ .

In terms of specific heat capacity we have

$$Q = m c_p(T_f - T_i)$$

$$Q = m c_v(T_f - T_i)$$

A very familiar result to us.

### Example 12

From the first law of thermodynamics show that

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v$$

**Solution**

According to first law, we have

$$dQ = dU + PdV$$

$U$  is function of either  $(T, V)$  or  $(T, P)$

Take

$$U = U(T, V)$$

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

$$\therefore dQ = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + PdV$$

Dividing throughout by  $dT$  we get

$$\frac{dQ}{dT} = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \frac{dV}{dT} + P \frac{dV}{dT}$$

At constant volume, we have

$$\left( \frac{dQ}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$

By definition L.H.S is the heat capacity at constant volume  $C_V$

$$\therefore C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

**Example 13**

Assuming that internal energy of a hydrostatic system is a function of  $T$  and  $P$ , show that  $\left( \frac{\partial U}{\partial T} \right)_P = C_p - PV\beta$ .

**Solution**

$$U = U(T, P) \text{ given}$$

Taking differentials on both sides, we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

From first law of thermodynamics, we have

$$dQ = dU + PdV$$

$$\text{or } dQ = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP + PdV$$

Dividing throughout by  $dT$  and keep  $P$  constant

$$\left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{dV}{dT}\right)_P$$

$$\text{i.e., } C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{dV}{dT}\right)_P$$

$$\text{Using } \beta = \frac{1}{V} \left(\frac{dV}{dT}\right)_P$$

$$\therefore \left(\frac{dV}{dT}\right)_P = \beta V$$

$$\text{Thus } C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\beta V$$

$$\text{or } \left(\frac{\partial U}{\partial T}\right)_P = C_P - P\beta V$$

### Example 14

Taking  $U$  to be a function of  $P$  and  $V$ , show that  $\left(\frac{\partial U}{\partial P}\right)_V = C_V \frac{k}{\beta}$

### Solution

$$U = U(P, V) \text{ given}$$

Taking differentials on bothsides, we get

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV$$

Using first law of thermodynamics

$$dQ = dU + PdV$$

$$\text{or } dQ = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV + PdV$$

Dividing throughout by  $dP$  and keep  $V$  constant, we get

$$\left(\frac{dQ}{dP}\right)_V = \left(\frac{\partial U}{\partial P}\right)_V \quad \dots\dots (0)$$

L.H.S can be written as

$$\left(\frac{dQ}{dP}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{dQ}{dP}\right)_V = C_V \left(\frac{\partial T}{\partial P}\right) \quad \dots\dots (1)$$

From the definition of  $k$  and  $\beta$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\beta V = \left(\frac{\partial V}{\partial T}\right)_P \quad \dots\dots (2)$$

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\text{or } kV = -\left(\frac{\partial V}{\partial P}\right)_T \quad \dots\dots (3)$$

$$\frac{\text{eq 3}}{\text{eq 2}} \text{ gives } \frac{k}{\beta} = -\left(\frac{\partial V}{\partial P}\right)_T \div \left(\frac{\partial V}{\partial T}\right)_P$$

or

$$\frac{k}{\beta} = - \left( \frac{\partial V}{\partial P} \right)_T \cdot \left( \frac{\partial T}{\partial V} \right)_P$$

$$\frac{k}{\beta} = \left( \frac{\partial T}{\partial P} \right)_V$$

Put this in equation (1), we get

$$\left( \frac{dQ}{dP} \right)_V = C_V \frac{k}{\beta}$$

$$\therefore \left( \frac{\partial U}{\partial P} \right)_V = C_V \frac{k}{\beta}.$$

### IMPORTANT FORMULAE

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1. Boyle's law:  $PV = \text{constant}$
2. Ideal gas equation :  $PV = nRT$
3. Expression for real gas temperature

$$\theta = 273.16K \frac{P}{P_{TP}}$$

4. Ideal gas temperature

$$T = 273.16K \underset{L \rightarrow P_{TP} \rightarrow 0}{\text{lt}} \frac{P}{P_{TP}}$$

5. Vander Waals equation of state

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

6. The coefficient of volume expansion

$$\beta = \frac{1}{V} \left( \frac{dV}{dT} \right)_P$$

7. Bulk modulus and compressibility

$$B = -V \left( \frac{\partial P}{\partial V} \right)_T$$

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T ; k_T = \frac{1}{B}$$

## 8. Theorems on partial derivative

$$(i) \quad \left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{(\partial y / \partial x)_z}$$

$$(ii) \quad \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x = - \left( \frac{\partial x}{\partial z} \right)_y$$

9. Relation between  $\beta$  and  $k$ 

$$\frac{\beta}{k} = \left( \frac{\partial P}{\partial T} \right)_V$$

$$10. \text{ Work done during a finite quasi-static process : } W = - \int_{V_i}^{V_f} P dV$$

If the work is positive work is done on the system.

If the work is negative work is done by the system.

## 11. Work done during an quasi-static isothermal process

$$W = -nRT \ln \frac{V_f}{V_i}$$

$$\text{or } W = -nRT \ln \frac{P_i}{P_f}$$

## 12. Work done during isothermal increase of pressure on a solid

$$W \approx \frac{kV}{2} (P_f^2 - P_i^2)$$

## 13. Work done during a quasi-static adiabatic process

$$W = \frac{1}{\gamma - 1} [P_f V_f - P_i V_i]$$

$$\text{or } W = \frac{nR}{\gamma - 1} (T_f - T_i)$$

$$14. \quad W_{i \rightarrow f} \text{ (adiabatic)} = U_f - U_i$$

## 15. First law of thermodynamics

$$U_f - U_i = Q + W$$

$$dU = dQ + dW \text{ Differential form}$$

16. Heat capacity

$$C = \frac{dQ}{dT} \text{ JK}^{-1}$$

17. Specific heat capacity

$$c = \frac{1}{m} \left( \frac{dQ}{dT} \right) \text{ J kg}^{-1} \text{ K}^{-1}$$

18. Molar heat capacity

$$c = \frac{1}{n} \left( \frac{dQ}{dT} \right) \text{ J mol}^{-1} \text{ K}^{-1}$$

19. Heat capacity at constant volume

$$C_v = \left( \frac{dQ}{dT} \right)_v = \left( \frac{\partial U}{\partial T} \right)_v$$

20. Heat capacity at constant pressure

$$C_p = \left( \frac{dQ}{dT} \right)_p$$

21. Heat in terms of  $C_p$  and  $C_v$

$$Q = mc_v(T_f - T_i)$$

$$Q = mc_p(T_f - T_i)$$

### UNIVERSITY MODEL QUESTIONS

#### Section A

(Answer questions in two or three sentences)

#### Short answer questions

1. What does thermodynamic deal with?
2. Define (i) system (ii) surroundings.
3. Define the following
  - (i) open system (ii) closed system
  - (iii) Isolated system.
4. Which are the two points of view adopted to study a system?

5. What is meant by macroscopic point of view?
6. What is meant by microscopic point of view?
7. What are macroscopic coordinates?
8. What are the properties of macroscopic coordinates?
9. What are the properties involved in the microscopic description of a system?
10. Define (i) Mechanical coordinates.  
(ii) Thermodynamic coordinates.
11. What is meant by equilibrium state of a system?
12. Define thermal equilibrium of a system.
13. Define thermal equilibrium of two systems separated by a diathermic wall.
14. What is an adiabatic wall? Give two examples.
15. What is a diathermic wall? Give an example.
16. State zeroth law of thermodynamics.
17. Define temperature.
18. Define triple point of water.
19. Write down the relation between real gas temperature ( $\theta$ ) and thermodynamic temperature ( $T$ ).
20. What is the principle of ideal gas thermometer?
21. Draw the labelled diagram of constant volume gas thermometer.
22. What are the advantages of using helium in constant volume gas thermometer? Under what conditions.
23. Under what conditions the ideal gas temperature and real gas temperature coincide.
24. A thermodynamic system is said to undergo change when?
25. What is meant by mechanical equilibrium of a system?
26. What is meant by chemical equilibrium of a system?
27. When a system is said to be in thermodynamic equilibrium?
28. Define a non-equilibrium state.
29. What is an equation of state?
30. What is the limitation of equation of state?
31. Write down any two equations of state and explain the symbols.
32. What is a hydrostatic system?
33. Define average
  - (i) coefficient of volume expansion
  - (ii) isothermal bulk modulus.

34. What is meant by compressibility of a system? What is its unit?
35. What is the importance of coefficient of volume expansion?
36. What is the importance of isothermal compressibility in thermodynamics?
37. What are intensive and extensive variables?
38. Distinguish between external work done and internal work done.
39. Write down the sign convention of work in consistent with mechanics.
40. What is a quasi-static process?
41. Write down an expression for work done by an hydrostatic system.
42. What is a PV diagram?
43. What are the indications of PV diagram?
44. Define temperature.
45. Define heat.
46. Distinguish between work and heat
47. Define (i) adiabatic wall and (ii) diathermic wall.
48. What is meant by adiabatic work?
49. Distinguish between adiabatic work and thermodynamic work.
50. What is meant by internal energy of a thermodynamic system?
51. What is the relation between adiabatic work and internal energy function?
52. Distinguish between diathermic work and adiabatic work.
53. State first law of thermodynamics.
54. What are the significance of first law of thermodynamics?
55. Define thermodynamic heat.
56. What are the sign conventions used in connection with first law of thermodynamics?
57. Change of heat is an in exact differential. Justify.
58. Why it is meaningless to say heat in a body or work in a body?
59. Write down the differential form of first law for a quasi-static process of a hydrostatic system.
60. What is meant by heat capacity?
61. Define average heat capacity and heat capacity.
62. Define specific heat capacity. What is its unit?
63. Define molar heat capacity. What is its unit?
64. Define the specific heat of a gas at (i) constant pressure and (ii) constant volume.
65. Explain why  $C_p > C_v$  for a gas.
66. Define 1 calorie of heat.

67. Define specific heat of water.
68. Show graphical variation of specific heat of water with temperature.
69. How to achieve quasi-static flow of heat?
70. What is a reservoir? Give two examples.

### Section B

(Answer questions in a paragraph of about half a page to one page)

#### Paragraph / Problem type

1. What are the properties of macroscopic coordinates and microscopic system?
2. Distinguish between macroscopic and microscopic points of view.
3. How equilibrium of two separate systems ( $X, Y$ ) and ( $X', Y'$ ) be defined?
4. Establish the concept of temperature on the basis of zeroth law of thermodynamics.
5. Explain how do you check whether or not two beakers of water are in equilibrium using zeroth law of thermodynamics.
6. Explain an hydrostatic system and classify it.
7. Show that hydrostatic work depends on paths.
8. Derive an expression for work done during an isothermal process.
9. Derive an expression for work done during isothermal increase of pressure on a solid.
10. Derive an expression for work done during quasi-static adiabatic process.
11. Derive an expression for work done during quasi-static isobaric process.
12. Show that work done during a quasi-static isochoric process is always zero.
13. Distinguish between heat and work.
14. Show that adiabatic work done is equal to the change in internal energy.
15. For an ideal gas show that  $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{kV}$  where  $k$  is the compressibility.
16. The equation of state of a Vander Waals gas is given as

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT, v = \frac{V}{vn}$$

where  $a, b$  and  $R$  are constants. Calculate

$$(a) \left(\frac{\partial P}{\partial v}\right)_T \quad (b) \left(\frac{\partial P}{\partial T}\right)_v$$

From parts a and b calculate  $\left(\frac{\partial v}{\partial T}\right)_P$

17. (a) A block of copper at a pressure of 1 atm ( $10^5$  Pa) and a temperature of  $5^\circ\text{C}$  is kept at constant volume. If the temperature is raised to  $10^\circ\text{C}$ , what will be the final pressure  $(4.02 \times 10^7$  Pa)
- (b) If the vessel holding the block of copper has a negligible thermal expansivity and can withstand a maximum pressure of 1000 atm, what is the highest temperature to which the system may be raised.

$$\beta = 4.95 \times 10^{-5} \text{ K}^{-1}, k = 6.17 \times (10^{-12} \text{ Pa})^{-1} \quad (17.45^\circ\text{C})$$

18. From the first law of thermodynamics show that  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_v}{V\beta} - P$ .

19. Assuming internal energy of a hydrostatic system is a function of T and P derive

$$\left(\frac{\partial U}{\partial P}\right)_T = PVk - (C_p - C_v)\frac{k}{\beta}.$$

20. Taking U to be a function of P and V show that  $\left(\frac{\partial U}{\partial V}\right)_P = \frac{C_p}{V\beta} - P$ .

### Section C

(Answer question in about two pages)

#### Long answer type questions - essays

- Explain how do you find ideal gas temperature using a constant volume gas thermometer.
- Explain the electrical method of measuring heat capacity.
- Starting from the quasistatic flow of heat explain how will you measure heat.

#### Hints to problems

15. Using  $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \dots\dots (1)$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{k} \text{ from example 1} \quad \dots\dots (2)$$

From the definition of  $\beta$ , we have

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

or  $\left(\frac{\partial V}{\partial T}\right)_P = \beta V \quad \dots\dots (3)$

Substituting eqs 2 and 3, we get the result

16. We have  $\left( P + \frac{a}{v^2} \right) (v - b) = RT$

$$P + \frac{a}{v^2} = \frac{RT}{v - b}$$

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

- a) Differentiate with respect to  $v$ , keeping  $T$  constant

$$\left( \frac{\partial P}{\partial v} \right)_T = -\frac{RT}{(v - b)^2} - \frac{2a}{v^3}$$

- b) Differentiate with respect to  $T$ , keeping  $v$  constant

$$\left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{v - b}$$

Using  $\left( \frac{\partial P}{\partial T} \right)_v \cdot \left( \frac{\partial T}{\partial v} \right)_P = -\left( \frac{\partial P}{\partial v} \right)_T$

$$\left( \frac{\partial P}{\partial v} \right)_P = +\frac{\frac{RT}{(v - b)^2} - \frac{2a}{v^3}}{R/v - b}$$

$$\left( \frac{\partial T}{\partial v} \right)_P = \frac{T}{(v - b)} - \frac{2a(v - b)}{Rv^3}$$

Usually product  $ab$  is negligibly small

$$\left( \frac{\partial T}{\partial v} \right)_P = \frac{T}{v - b} - \frac{2a}{v^2 R}$$

$$\left( \frac{\partial T}{\partial v} \right)_P = \frac{v^2 RT - 2a(v - b)}{(v - b)v^2 R}$$

$$\left( \frac{\partial T}{\partial v} \right)_P = \frac{v^2 RT - 2aV}{(v - b)V^2 R}$$

Inverting we get the required result.

17. a) Use  $P_f - P_i = \frac{\beta}{k}(T_f - T_i)$ , get the result

b)  $\frac{\beta}{k} = \frac{4.95 \times 10^{-5}}{6.17 \times 10^{-12}} = 80.23 \times 10^5 \text{ Pa}$

$$(1000 - 1) = 80.23(T_f - 278)$$

$$T_f - 278 + \frac{999}{80.23} = 12.45$$

$$T_f = 278 + 12.45 = 290.45$$

$$T_f = 17.45^\circ\text{C}$$

18. From example 12, we have

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P dV$$

Dividing throughout by  $dT$  keeping  $P$  constant

$$\left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{dT}\right)_P + P \left(\frac{dV}{dT}\right)_P$$

$$\text{i.e., } C_P = C_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) \left(\frac{dV}{dT}\right)_P \quad \dots\dots (1)$$

From the definition  $\beta$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

Substituting for  $\left(\frac{\partial V}{\partial T}\right)_P$  in eq (1) we get

$$C_P = C_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) \beta V$$

$$\text{or } \left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V\beta} - P$$

19. See example 14, only a slight change

20. See example 15, only slightly different.

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